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Continued on last page

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(54) [Title of the Invention] Contact Lens Material Comprised of Hydrophilic Polysiloxane Monomers and Copolymers Thereof and Contact Lenses

(57) [Abstract]

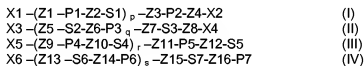
[Problem] To provide a lens material for eyeglasses that is strong, that has sufficient surface hydrophilicity, that is of high oxygen permeability and that is of superior contamination resistance.

[Means of Solution] A hydrophilic polysiloxane monomer which is a monomer that has polymerizable unsaturated groups in the terminals of a structure in which at least polysiloxane groups and polyoxyalkylene groups are linked characterized in that it has two or more polymerizable unsaturated groups in at least one terminal and a contact lens material comprised of said monomer and a contact lens.

[Claims]

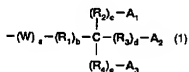
[Claim 1] A hydrophilic polysiloxane monomer which is a monomer that has polymerizable unsaturated groups in the terminals of a structure in which at least polysiloxane groups and polyoxyalkylene groups are linked characterized in that it has two or more polymerizable unsaturated groups in at least one terminal.

[Claim 2] A hydrophilic polysiloxane monomer as described in Claim 1 that is selected from formulas (I) and (II), (III) and (IV).

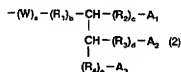


[Wherein, p and q are 1 ~ 10. r and s are 0 ~ 10. X1 and X2, X3, X4 are independent and are selected from Formula (1), Formula (2) and Formula (3) below. At least one of (X1 or X2 is Formula (1) or (2) below and at least one of X3 or X4 is Formula (1) or (2) below. X5 and X6 indicate Formula (1) or (2) below.

[Chemical Formula 1]



[Chemical Formula 2]



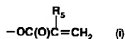
[Chemical Formula 3]



(Each a and b, c, d, e<sup>1</sup> is independent and are 0 or 1. Each W is independent and is -O- or -NR<sub>5</sub>-. R<sub>1</sub> and R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> are independent and are chain hydrocarbon groups of 1 to 10 carbon atoms that may be interrupted at any one or more points by amide groups, urethane groups, urea groups, oxy groups, ester groups, carbonyl groups, aryl groups, and alicyclic hydrocarbon groups of 5 to 7 carbon atoms. The above described chain hydrocarbon groups of 1 to 10 carbon atoms may be substituted at any desired individual point or more points by aryl groups and the alicyclic hydrocarbon groups of 5 to 7 carbon atoms may be similarly substituted by alkyl groups of 1 to 4 carbon atoms, fluoro groups, fluoro-substituted

hydrocarbon groups of 1 to 10 carbon atoms and hydroxyl groups.  $A_1$  and  $A_2$ ,  $A_3$  are independent and are hydrogen, hydroxyl groups, methyl groups or any of formulas (i), (ii) or (iii). At least two of  $A_1$  and  $A_2$ ,  $A_3$  may be selected from formulas (i), (ii) or (iii) and may be the same or different.  $A_4$  is selected from formulas (i), (ii) and (iii).

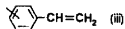
[Chemical Formula 4]



[Chemical Formula 5]



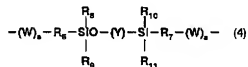
[Chemical Formula 6]



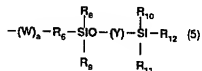
Wherein,  $R_5$  is independent and is hydrogen or a hydrocarbon group of 1 to 4 carbon atoms.)

S1 and S2, S3, S4, S6, S7 are independent and are polysiloxane groups indicated by chemical formula (4). S5 is a polysiloxane group indicated by chemical formula (5).

[Chemical Formula 7]

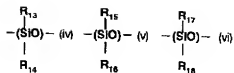


[Chemical Formula 8]



(Each  $R_6$  and  $R_7$  is independent and is a chain hydrocarbon group of 1 to 30 carbon atoms that may be interrupted at any one or more points by amide groups, urethane groups, urea groups, oxy groups, ester groups, carbonyl groups, aryl groups, and alicyclic hydrocarbon groups of 5 to 7 carbon atoms. The above described chain hydrocarbon groups of 1 to 30 carbon atoms may be substituted at any desired individual point or more points by aryl groups and the alicyclic hydrocarbon groups of 5 to 7 carbon atoms may be similarly substituted by alkyl groups of 1 to 4 carbon atoms, fluoro groups, fluoro-substituted hydrocarbon groups of 1 to 10 carbon atoms and hydroxyl groups.  $R_8$  and  $R_9$ ,  $R_{10}$ ,  $R_{11}$  and  $R_{12}$  are groups that have been substituted by hydrocarbon groups of 1 to 12 carbon atoms or trimethyl siloxane groups and may be the same or different. Y links the structural units (iv), (v) and (vi) indicated in the formula below. The number of links of (iv), (v) and (vi) is 1 to 1000 and (v) and (vi) may be 0.

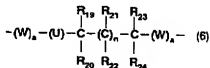
[Chemical Formula 9]



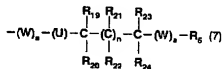
Wherein, R<sub>13</sub> and R<sub>14</sub> are independent and are hydrocarbon groups of 1 to 12 carbon atoms or trimethyl siloxane groups. R<sub>15</sub> and R<sub>16</sub> are hydrocarbon groups of 1 to 12 carbon atoms, trimethyl siloxane groups or fluoro-substituted hydrocarbon groups of 1 to 12 carbon atoms. At least one of R<sub>15</sub> or R<sub>16</sub> is a fluoro group substituted hydrocarbon group. R<sub>17</sub> and R<sub>18</sub> are independent and are groups comprised of hydrocarbon groups of 1 to 12 carbon atoms, trimethyl siloxane groups or hydrophilic substituted groups. At least one of R<sub>17</sub> or R<sub>18</sub> is a hydrophilic substituted group. Here, the term hydrophilic substituted group refers to a chain or cyclic hydrocarbon group in which at least one group selected from carboxylic acid groups, amino groups, imino groups, amide groups or oxyalkylene groups is bonded.)

P1 and P2, P3, P4, P5, P6 are independent and are polyoxyalkylene groups indicated by formula (6). P7 is a polyoxyalkylene group indicated by formula (7).

[Chemical Formula 10]

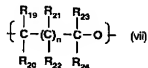


[Chemical Formula 11]



(Wherein, U is a link of the structural formula (vii) indicated by the formula below. The number of links is 1 to 200.

[Chemical Formula 12]



Wherein, each R<sub>19</sub> and R<sub>20</sub>, R<sub>21</sub>, R<sub>22</sub>, R<sub>23</sub>, R<sub>24</sub> is independent and are hydrogen, fluoro groups, hydrocarbon groups of 1 to 10 carbon atoms, fluoro-substituted hydrocarbon groups of 1 to 10 carbon atoms and aryl groups. n is 0 ~ 4.)

Z1 and Z2-Z16 are independent and are linking groups indicated by formulas (5a), (5b) and (5c).

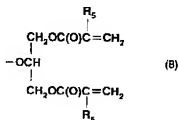
LR<sub>6</sub>L (5a)LR<sub>5</sub> (5b)R<sub>6</sub>L (5c)

(Wherein, L is -C(O)NR<sub>3</sub>-, -NR<sub>3</sub>C(O)-, -C(O)O-, -OC(O)-, or -C(O)-.)]

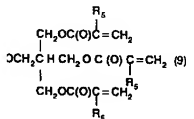
[Claim 3] A hydrophilic polysiloxane monomer as described in Claim 2 in which p and q in formula (I) and formula (II) are selected from 1 and r and s in formula (III) and formula (IV) are selected from 0.

[Claim 4] A hydrophilic polysiloxane monomer as described in Claims 2 or 3 in which X1 and X2, X3, X4 in formula (I) and formula (II) are selected from formulas (8), (9) or (10). However, at least 1 of X1 and X2 is formula (8) or (9) and at least one of X3 and X4 is formula (8) or (9).

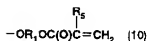
[Chemical Formula 13]



[Chemical Formula 14]

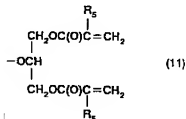


[Chemical Formula 15]

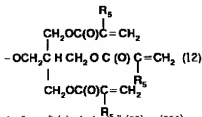


[Claim 15] A hydrophilic polysiloxane monomer as described in Claims 2 or 3 in which X5 and X6 in formula (III) and formula (IV) are selected from formula (11) or (12).

[Chemical Formula 16]

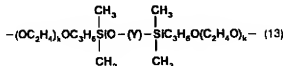


[Chemical Formula 17]

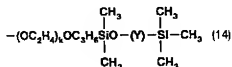


[Claim 6] A hydrophilic polysiloxane monomer as described in any one of Claims 2 to 5 in which S1 and S2, S3, S4, S6, S7 in formulas (I) and (II), (III), (IV) are selected from polysiloxane groups of formula (14) and S5 is selected from the polysiloxane groups of formula (14).

[Chemical Formula 18]



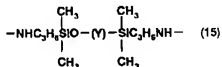
[Chemical Formula 19]



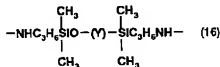
(Wherein, k is 0 ~ 4)

[Claim 7] A hydrophilic polysiloxane monomer as described in any one of Claims 2 to 5 in which S1 and S2, S3, S4, S6, S7 in formula (I) and formulas (II), (III), (IV) are selected from polysiloxane groups of formula (15) and S5 is selected from formula (16).

[Chemical Formula 20]

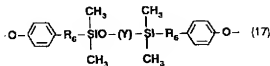


[Chemical Formula 21]

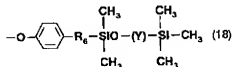


[Claim 8] A hydrophilic polysiloxane monomer as described in any one of Claims 2 to 5 in which S1 and S2, S3, S4, S6, S7 in formula (I) and formulas (II), (III), (IV) are selected from polysiloxane groups of formula (17) and S5 is selected from formula (18).

[Chemical Formula 22]

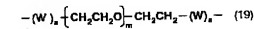


[Chemical Formula 23]

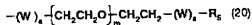


[Claim 9] A hydrophilic polysiloxane monomer as described in any one of Claims 2 to 8 in which P1 and P2, P3, P4, P6 in formula (I) and formulas (II), (III), (IV) are selected from polyoxysiloxane groups of formula (19) and P7 is selected from formula (20).

[Chemical Formula 24]

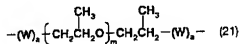


[Chemical Formula 25]

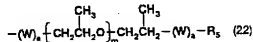


[Claim 10] A hydrophilic polysiloxane monomer as described in any one of Claims 2 to 8 in which P1 and P2, P3, P4, P6 in formula (I) and formulas (II), (III), (IV) are selected from polyoxysiloxane groups of formula (21) and P7 is selected from formula (22).

[Chemical Formula 26]



[Chemical Formula 27]



[Claim 11] A hydrophilic polysiloxane monomer as described in any one of Claims 2 to 10 in which Z1 and Z2 ~ S16 are selected from formula (23).

[Chemical Formula 28]



[Claim 12] A (co) polymer obtained by polymerizing a polymerizable composition that contains at least one or more types of hydrophilic polysiloxane monomers as described in any one of Claims 1 to 11.

[Claim 13] A copolymer that is obtained by polymerizing a polymerizable composition that contains at least one or more types of hydrophilic polysiloxane monomers as described in any one of Claims 1 to 11 and one or more copolymerizable monomers.

[Claim 14] A copolymerizable monomer that is obtained by polymerizing a polymerizable composition that contains at least one or more types of hydrophilic polysiloxane monomers as described in any one of Claims 1 to 11 and one or more copolymerizable monomers.

[Claim 15] The copolymers of Claim 13 and Claim 14 of which the copolymerizable monomer is selected from at least one type of hydrophilic monomer.

[Claim 16] The copolymer of Claim 15 of which the hydrophilic monomer has an amide group.

[Claim 17] The copolymer of Claim 16 of which the hydrophilic monomer that has an amide group is N,N-dimethyl acrylamide, N-vinyl pyrrolidone and N-methyl N-vinyl acetamide.

[Claim 18] Copolymers as described in any one of Claim 14 to Claim 17 of which the solvents not involved in polymerization are selected from one or more types of hydrophilic solvents.

[Claim 19] Copolymers as described in Claim 18 of which the hydrophilic solvent is selected from alcohols, ketones, ethers, esters, carboxylic acids, sulfoxides, amines, amides and nitrile compounds.

[Claim 20] Copolymers as described in Claim 19 of which the hydrophilic solvent is selected from butanol, hexanol, methyl ethyl ketone, tetrahydrofuran, ethyl acetate, dimethyl sulfoxide, N,N-dimethylformamide, and acetonitrile.

[Claim 21] A composition for ophthalmologic use that is comprised of (co) polymers as described in any one of Claim 12 to Claim 20.

[Claim 22] A lens for ophthalmologic use that is comprised of (co) polymers as described in any one of Claim 12 to Claim 20.

[Claim 23] A contact lens comprised of (co) polymers as described in any one of Claim 12 to Claim 20.

[Claim 24] A water-containing contact lens comprised of (co) polymers as described in any one of Claim 12 to Claim 20.

[Claim 25] A contact lens as described in Claim 23 or Claim 24 of which the (co) polymer composition is polymerized in lens shape in a mold.

[Claim 26] A contact lens as described in Claim 25 that is polymerized in a mold that is selected from a resin of which the angle of contact with the water in the liquid drop method is less than 90°.

[Claim 27] A contact lens as described in Claim 26 that is polymerized in a mold that is selected from a resin of which the angle of contact with the water in the liquid drop method is less than 65° ~ 80°.

[Claim 28] A contact lens as described in Claim 25 that is comprised of a resin the mold for which is selected from polyamide, polyethylene terephthalate and ethylene vinyl alcohol copolymer.

[Detailed Description of the Invention]

[0001]

[Field of use of the invention] This invention relates to a lens material for ophthalmologic use comprised of copolymers of which hydrophilic polysiloxanes are the principal constituents. In further detail, it related to hydrophilic copolymers of superior water wetting properties, oxygen permeability, contamination resistance, softness, optical transparency and strength that are useful as lenses for ophthalmologic use such as contact lenses.

[0002]

[Prior art] Polysiloxane compounds, of which dimethyl silicone compounds are representative display unique properties such as heat resistance, chemical stability, electric insulating properties, softness, lubricity and water repellency and are widely used industrially either alone or for modifying other materials. For example, polydimethyl siloxane, which is a polymerizable polysiloxane compound and which has methacryl groups in both terminals, is used for modification of polymers such as acrylic polymers and polystyrene utilizing its polymerizability. In addition, because polysiloxane polymers exhibit high gas permeability, they are also used as selective permeable membranes for gases. For example, studies have been made of their application to contact lenses making use of their superior oxygen permeability, softness and optical transparency and many patents have been proposed (for example,



Japanese Patent No. 1430546, Japanese Patent Application Early Disclosure No. Sho 63-29741 [1988], Japanese Patent No. 2532406 and Japanese Patent No. 2716181).

[0003] Contact Lenses are divided primarily into hard contact lenses and soft contact lenses. Although hard contact lenses are hard and are of poor wearing comfort, in recent years, there has been a marked improvement in their oxygen permeability and almost all of them are products that can be worn continuously. On the other hand, although soft contact lenses are soft and are comfortable to wear, there are various problems with them. Water-containing soft contact lenses are of poor oxygen permeability and durability, are easily damaged and present the danger of bacterial growth, for which reason periodic disinfection is necessary and they are frequently inconvenient to handle. Although some improvements have been made in water-containing soft contact lenses, their oxygen permeability is still not sufficient and they are not satisfactory as lenses for long-term wearing. Non-water-containing soft contact lenses are far inferior to water-containing lenses in terms of lens contamination, and contamination by lipids in particular.

[0004] In recent years, water-containing soft contact lenses of which hydrophilic siloxanes are the principal constituent and that are of high oxygen permeability, soft and of good wearing comfort have been developed (Japanese Patent No. 2938131). However, because sufficient hydrophilicity cannot be obtained on the lens surface, the wetting properties of tear solutions are poor and hydrophilic treatments of the surface such as prism treatment and hydrophilic monomer grafting are performed. Nevertheless, sufficient hydrophilicity and durability cannot be obtained by these treatments. In addition, because hydrophilic polysiloxane monomers have high molecular weights, a sufficient degree of crosslinking density cannot be obtained in the polymerization composition, there is poor mechanical strength and they are extremely easily damaged. In addition, it is a material that allows lipids to osmose into the interior of the lens and contaminate it.

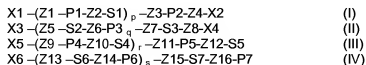
[0005]

[Problems the invention is intended to solve] Accordingly, the objective of this invention is to provide a lens for ophthalmologic use whereby the above-described drawbacks are eliminated, i.e., that, in spite of the fact that it exhibits high oxygen permeability, it has sufficient surface wetting properties and is of high strength and superior contamination resistance.

[0006]

[Means for solving the problems] The inventors conducted intensive research, and, as the result, arrived at this invention by discovering that hydrophilic polysiloxane monomers which are monomers that have polymerizable unsaturated groups in their terminals in which at least polysiloxane groups and polyoxyalkylene groups are linked and which are characterized in having two or more polymerizable unsaturated groups in at least one of their terminals are extremely effective for eliminating the above-described problems. Specifically, it provides lenses for ophthalmologic use as contact lenses that are comprised of hydrophilic polysiloxane monomers which are monomers that have polymerizable unsaturated groups in their terminals in which at least polysiloxane groups and polyoxyalkylene groups are linked and which are characterized in having two or more polymerizable unsaturated groups in at least one of their terminals and (co) polymers thereof.

[0007] The specific hydrophilic polyoxysilane monomers are represented by formula (I) or formulas (II), (III), (IV).

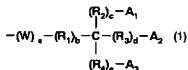


[Wherein, p and q are 1 ~ 10. r and s are 0 ~ 10. X1 and X2, X3, X4 are independent and are selected from Formula (1), Formula (2) and Formula (3) below. At least one of (X1 or X2 is Formula (1) or (2)

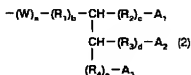
below and at least one of X3 or X4 is Formula (1) or (2) below. X5 and X6 indicate Formula (1) or (2) below.

[0008]

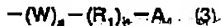
[Chemical Formula 29]



[Chemical Formula 30]



[Chemical Formula 31]

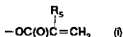


(Each a and b, c, d, e is independent and are 0 or 1. Each W is independent and is -O- or -NR<sub>5</sub>-.

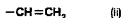
[0009] R<sub>1</sub> and R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> are independent and are amide groups or chain hydrocarbon groups of 1 to 10 carbon atoms that may be interrupted at any one or more points by urethane groups, urea groups, oxy groups, ester groups, carbonyl groups, aryl groups, and alicyclic hydrocarbon groups of 5 to 7 carbon atoms. The above described chain hydrocarbon groups of 1 to 10 carbon atoms may be substituted at any desired individual point or more points by aryl groups and the alicyclic hydrocarbon groups of 5 to 7 carbon atoms may be similarly substituted by alkyl groups of 1 to 4 carbon atoms, fluoro groups, fluoro-substituted hydrocarbon groups of 1 to 10 carbon atoms and hydroxyl groups.

[0010] A<sub>1</sub> and A<sub>2</sub>, A<sub>3</sub> are independent and are hydrogen, hydroxyl groups, methyl groups or any of formulas (i), (ii) or (iii). At least two of A<sub>1</sub> and A<sub>2</sub>, A<sub>3</sub> may be selected from formulas (i), (ii) or (iii) and may be the same or different. A<sub>4</sub> is selected from formulas (i), (ii) and (iii).

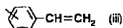
[Chemical Formula 32]



[Chemical Formula 33]



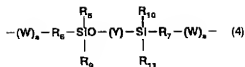
[Chemical Formula 34]



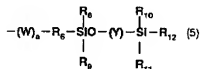
Wherein, R<sub>5</sub> is independent and is hydrogen or a hydrocarbon group of 1 to 4 carbon atoms.) S1 and S2, S3, S4, S6, S7 are independent and are polysiloxane groups indicated by chemical formula (4).

[0011] In addition, S5 is a polysiloxane group indicated by chemical formula (5).

[Chemical Formula 35]



[Chemical Formula 36]

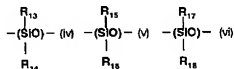


(Each  $R_6$  and  $R_7$  is independent and is a chain hydrocarbon group of 1 to 30 carbon atoms that may be interrupted at any one or more points by amide groups, urethane groups, urea groups, oxy groups, ester groups, carbonyl groups, aryl groups, and alicyclic hydrocarbon groups of 5 to 7 carbon atoms. The above described chain hydrocarbon groups of 1 to 30 carbon atoms may be substituted at any desired individual point or more points by aryl groups and the alicyclic hydrocarbon groups of 5 to 7 carbon atoms may be similarly substituted by alkyl groups of 1 to 4 carbon atoms, fluoro groups, fluoro-substituted hydrocarbon groups of 1 to 10 carbon atoms and hydroxyl groups.

[0012]  $R_8$  and  $R_9$ ,  $R_{10}$ ,  $R_{11}$  and  $R_{12}$  are groups that have been substituted by hydrocarbon groups of 1 to 12 carbon atoms or trimethyl siloxane groups and may be the same or different.  $Y$  links the structural units (iv), (v) and (vi) indicated in the formula below. The number of links of (iv), (v) and (vi) is 1 to 1000 and (v) and (vi) may be 0.

[0013]

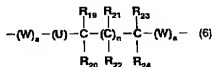
[Chemical Formula 37]



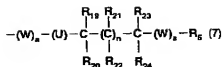
Wherein,  $R_{13}$  and  $R_{14}$  are independent and are hydrocarbon groups of 1 to 12 carbon atoms or trimethyl siloxane groups.  $R_{15}$  and  $R_{16}$  are hydrocarbon groups of 1 to 12 carbon atoms, trimethyl siloxane groups or fluoro-substituted hydrocarbon groups of 1 to 12 carbon atoms. At least one of  $R_{15}$  or  $R_{16}$  is a fluoro group substituted hydrocarbon group.  $R_{17}$  and  $R_{18}$  are independent and are groups comprised of hydrocarbon groups of 1 to 12 carbon atoms, trimethyl siloxane groups or hydrophilic substituted groups. At least one of  $R_{17}$  or  $R_{18}$  is a hydrophilic substituted group. Here, the term hydrophilic substituted group refers to a chain or cyclic hydrocarbon group in which at least one group selected from carboxylic acid groups, amino groups, imino groups, amide groups or oxyalkylene groups is bonded.)

[0014]  $P_1$  and  $P_2$ ,  $P_3$ ,  $P_4$ ,  $P_5$ ,  $P_6$  are independent and are polyoxyalkylene groups indicated by formula (6).  $P_7$  is a polyoxyalkylene group indicated by formula (7).

[Chemical Formula 38]

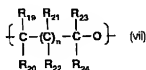


[Chemical Formula 39]



[0015] (Wherein, U is a link of the structural formula (vii) indicated by the formula below. The number of links is 1 to 200.

[Chemical Formula 40]



Wherein, each  $R_{19}$  and  $R_{20}$ ,  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$ ,  $R_{24}$  is independent and are hydrogen, fluoro groups, hydrocarbon groups of 1 to 10 carbon atoms, fluoro-substituted hydrocarbon groups of 1 to 10 carbon atoms and aryl groups.  $n$  is 0 ~ 4.)

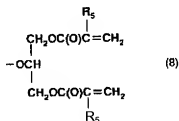
[0016]  $Z_1$  and  $Z_2$ - $Z_{16}$  are independent and are linking groups indicated by formulas (5a), (5b) and (5c).

 $LR_6L \quad (5a)$ 
 $LR_6 \quad (5b)$ 
 $R_6L \quad (5c)$ 

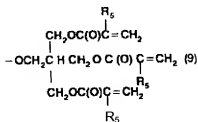
(Wherein, L is  $-C(O)NR_5-$ ,  $-NR_5C(O)-$ ,  $-C(O)O-$ ,  $-OC(O)-$  or  $OC(O)-$ .)

[0017] The inventions indicated below are included in this invention. A hydrophilic polysiloxane monomer in which  $p$  and  $q$  in formula (I) and formula (II) are selected from 1 and  $r$  and  $s$  in formula (III) and formula (IV) are selected from 0. A hydrophilic polysiloxane monomer in which  $X_1$  and  $X_2$ ,  $X_3$ ,  $X_4$  in formula (I) and formula (II) are selected from formulas (8), (9) or (10). However, at least 1 of  $X_1$  and  $X_2$  is formula (8) or (9) and at least one of  $X_3$  and  $X_4$  is formula (8) or (9).

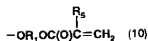
[Chemical Formula 41]



[Chemical Formula 42]

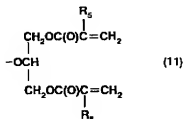


[Chemical Formula 43]

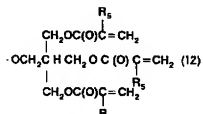


[0018] A hydrophilic polysiloxane monomer in which X5 and X6 in formula (III) and formula (IV) are selected from formula (11) or (12).

[Chemical Formula 44]

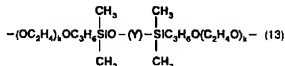


[Chemical Formula 45]

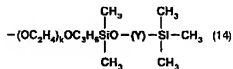


[0019] A hydrophilic polysiloxane monomer in which S1 and S2, S3, S4, S6, S7 in formulas (I) and (II), (III), (IV) are selected from polysiloxane groups of formula (14) and S5 is selected from the polysiloxane groups of formula (14).

[Chemical Formula 46]



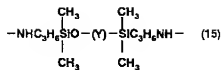
[Chemical Formula 47]



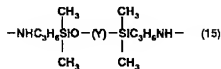
(Wherein, k is 0 ~ 4)

[0020] A hydrophilic polysiloxane monomer in which S1 and S2, S3, S4, S6, S7 in formula (I) and formulas (II), (III), (IV) are selected from polysiloxane groups of formula (15) and S5 is selected from formula (16).

[Chemical Formula 48]

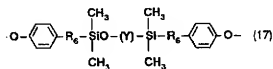


[Chemical Formula 49]

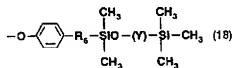


[0021] A hydrophilic polysiloxane monomer in which S1 and S2, S3, S4, S6, S7 in formula (I) and formulas (II), (III), (IV) are selected from polysiloxane groups of formula (17) and S5 is selected from formula (18).

[Chemical Formula 50]

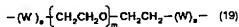


[Chemical Formula 51]

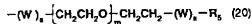


[0022] A hydrophilic polysiloxane monomer in which P1 and P2, P3, P4, P6 in formula (I) and formulas (II), (III), (IV) are selected from polyoxysiloxane groups of formula (19) and P7 is selected from formula (20).

[Chemical Formula 52]

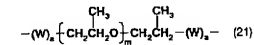


[Chemical Formula 53]

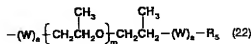


[0023] A hydrophilic polysiloxane monomer in which P1 and P2, P3, P4, P6 in formula (I) and formulas (II), (III), (IV) are selected from polyoxysiloxane groups of formula (21) and P7 is selected from formula (22).

[Chemical Formula 54]



[Chemical Formula 55]



[0024] A hydrophilic polysiloxane monomer in which Z1 and Z2 ~ S16 are selected from formula (23).

[Chemical Formula 56]



[0025] The number of links of the polysiloxane groups and the polyoxyalkylene groups in the molecule of the hydrophilic polysiloxane monomers of this invention is important. When the number of links of polysiloxane groups is relatively great, oxygen permeability is increased but hydrophilicity is decreased and lipid contamination is increased. When the number of links of polyoxyethylene groups is relative great, the converse phenomena occur. Thus, it is desirable to select from siloxane groups of which the total number of Y is 10 to 200 and polyoxyalkylene groups of which the total number of U is 2 to 50.

[0026] Several methods of synthesis of the hydrophilic polysiloxane monomers disclosed in this invention can be considered. Examples include the following methods.

Isocyanate modified polyoxyalkylene derivatives are synthesized by reacting polyoxyalkylene derivatives of various molecular weights having hydroxyl groups in their terminals such as polyethylene glycol, polypropylene glycol or polyethylene glycol and polypropylene glycol block copolymers with diisocyanate compounds such as hexamethylene diisocyanate, isophorone diisocyanate, toluene diisocyanate, xylylene diisocyanate and naphthalene diisocyanate. Next, polysiloxane compounds modified by isocyanates in which the terminals are carbinal, amines and phenols and by functional groups are reacted with isocyanate modified polyoxyalkylene derivatives. At this time, the reaction can be carried out with good efficiency when catalysts such as dibutyltin dilaurate, stannous chloride, triethylamine and diethylene triamine are used in combination.

[0027] In addition, by changing the charging ratios of the polysiloxane compounds and isocyanate modified polyoxyalkylene derivatives, the quantity of repeating units of polysiloxane and polyoxyalkylene derivatives in the molecule can be regulated. Next, isocyanate derivatives such as glycerol dimethacrylate, 3-acryloyl oxyglycerol monomethacrylate and pentaerythritol triacrylate, polymerizable compounds with reactive functional groups, and, depending on the circumstances, compounds obtained by reacting the above described polymerizable compounds with reactive functional groups in advance with isocyanate compounds are introduced into the reaction solution. In addition, mixtures of monofunctional polymerizable compounds such as 2-hydroxyethyl methacrylate and isocyanatoethyl methacrylate with the above described polyfunctional polymerizable compounds can also be used.

[0028] The lens materials for ophthalmologic use of this invention are comprised of copolymers that are obtained by copolymerizing one or two or more of the hydrophilic polysiloxane monomers represented by formulas (I) and (II), (III), (IV with only said hydrophilic polysiloxane monomers or with one or more copolymerizable monomers. In order to constitute good hydrophilic polysiloxane monomers, they are selected as indicated below in accordance with the target properties of the lens material for ophthalmologic use, for example, the required oxygen permeability, softness, difficulty of attachment of soiling, strength and water content ratio. Specifically, these are the number and type of reactive double bond groups in the monomer, the type of units and number of links that constitute Y of the polysiloxane group and the type and number of links of the units that constitute the polyoxyalkylene group. The copolymers comprised of hydrophilic polysiloxane monomers that are disclosed in this invention that are used include, of course, water containing compositions of which the water content ratio exceeds 1% and also compositions that essentially do not contain water with water content ratios less than 1%. That is, both water-containing soft lens materials and non-water containing soft lens materials can be used as the contact lens materials. They are also useful for intraocular lenses which consist of other lens materials for ophthalmologic use.

[0029] Here, we shall now explain the copolymerizable monomers. Although any monomer can be used in this invention as long as it is copolymerizable, hydrophilic monomers are especially useful.

They can be used as monomers for further increasing the surface wetting properties of the polymer and for changing the water content ratio. For example, they can include monomers containing hydroxyl groups such as 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 4-hydroxybutyl acrylate, and glycerol methacrylate, hydroxyl group containing monomers that have fluorine substitution groups such as 3-(1,1,2,2-tetrafluoroethoxy)-2-hydroxypropyl methacrylate, monomers containing carboxylic acid groups such as methacrylic acid, acrylic acid and itaconic acid, monomers containing alkyl substituted amino groups such as dimethylaminoethyl methacrylate and diethylaminoethyl methacrylate, and, further, monomers containing oxyalkylene groups such as methoxypolyethylene glycol monomethacrylate and polypropylene glycol monoacrylate. Preferably, monomers containing amide groups or imide groups such as N,N-dimethyl acrylamide, N,N-diethylacrylamide, N-methylacrylamide, methylene bis acrylamide, diacetone acrylamide and N-vinyl pyrrolidone can increase the hydrophilicity of the contact lens more effectively. More preferably, by selecting N,N-dimethyl acrylamide, N-methyl N-vinyl acetamide and N-vinyl pyrrolidone, a transparent copolymer with markedly better surface wetting properties can be obtained.

[0030] To present one example of other monomers that can be used, they can include fluorine-containing monomers such as acrylic acid fluoroalkyl esters and methacrylic acid fluoroalkyl esters, for example, trifluoroethyl acrylate, tetrafluoroethyl acrylate, tetrafluoropropyl acrylate, pentafluoropropyl acrylate, hexafluoroisobutyl acrylate, hexafluoroisopropyl acrylate and methacrylates corresponding to these acrylates. They can be selected in accordance with the required compatibility, hydrophilicity, water content ratio and contamination resistance.

[0031] In addition, so-called siloxanyl acrylates are also useful copolymerization monomers for regulating oxygen permeability. For example, they include tris (trimethylsiloxy) silyl propyl methacrylate, bis (trimethylsiloxy) methyl silyl propyl methacrylate and pentamethyl disiloxanyl methacrylate. Moreover, copolymerizable polydimethyl siloxanes in which methacrylate groups are substituted can also be used for similar objectives.

[0032] In addition, as required, acrylic acid alkyl ester monomers and methacrylic acid alkyl ester monomers can be used as required. To cite one example, they can be methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, tert-butyl acrylate, cyclopentyl acrylate, cyclohexyl acrylate, n-stearyl acrylate and methacrylates corresponding to these acrylates.

[0033] As required, the monomers described below can be copolymerized in order to improve mechanical properties and dimensional stability. Monomers for improving mechanical properties can include, for example, aromatic vinyl compounds such as styrene, tert-butyl styrene and  $\alpha$ -methyl styrene. In addition, monomers for increasing dimensional stability can include, for example, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, trimethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, trimethylol propane trimethacrylate, pentaerythritol tetramethacrylate, bisphenol A dimethacrylate, vinyl methacrylate, acrylic methacrylate and acrylate corresponding to these methacrylates, divinyl benzene and triallyl isocyanurate. One of these monomers or combinations of two or more may be used.

[0034] Mixed monomers containing these copolymerizable monomers can be used for the purpose of improving the balance of such characteristics of said copolymers as their optical characteristics, oxygen permeability, mechanical strength, attachment of soiling when worn in the eyes, dimensional stability in tears and changes in them over time. Moreover, as required, various additives may be added before polymerization or after polymerization. Additives can be, for example, various colorants, UV absorbents and antioxidants.

[0035] The copolymers that are used as materials for ophthalmologic use in this invention can be molded into lenses for ophthalmologic use, for example, by the so-called mold molding method in which the mold is filled with a mixture of hydrophilic polysiloxane monomer and hydrophilic monomer and the mixture is subjected to radical polymerization by a known method and the so-called spin casting method in which the monomer mixture is introduced into a rotating hemispherical mold and is polymerized. Substances in which the monomers exhibit good solubility can be used as the solvents that are added.



For example, alcohols, ketones, ethers, esters, carboxylic acids, sulfoxides, amines, amides, and nitrile compounds can be selected. Preferably, the solvents that can be used are changed depending on the combinations of hydrophilic polysiloxane monomers and copolymerizable monomers. When butanol, hexanol, methyl ethyl ketone, tetrahydrofuran, ethyl acetate, dimethyl sulfoxide, N,N-dimethyl formamide and acetonitrile are selected, peeling from the mold after polymerization is facilitated, water wetting properties are good and a transparent contact lens can be manufactured. These solvents can be added in proportions accounting for 1% to 99% of the polymerizable composition. Preferably, manufacture of contact lenses of good dimensional stability and water wetting properties is possible when 10% to 90%, and, more preferably, 20% to 80%, is added.

[0036] Mold materials that are used in the mold polymerization method and the cast polymerization method can be used as long as they are essentially insoluble in the monomer mixture and the lens can be peeled off after polymerization. For example, polyolefin resins such as polypropylene and polyethylene can be used. Preferably, materials that have polar groups on the surface and that have a small angle of contact with water are suitable. The term polar groups refers to atomic groups that have strong affinity for water and indicates hydroxyl groups, nitrile groups, carboxyl groups, polyoxyethylene groups, amide groups and urethane groups. Desirable mold materials are insoluble in the polymerization monomer compositions. Further, the component of the mold that forms at least one lens face is a substance of which the angle of contact with water is less than  $90^\circ$  as determined by the liquid drop method.

[0037] More preferably, it is a substance of which the angle of contact with water is  $65^\circ$  to  $80^\circ$  as determined by the liquid drop method. Lenses that are molded using molds of an angle of contact with the surface of the mold material of less than  $80^\circ$  are of particularly good water wetting properties and exhibit stable properties such as lipid attachment. In addition, with materials that exhibit angles of contact less than  $65^\circ\text{C}$ , separation of the lens and mold material is difficult, minute damage to the surface and chips in the edge parts are readily brought about and are not practical. More preferably, the mold material should be a resin selected from polyamides, polyethylene terephthalate and ethylene vinyl alcohol copolymers. In particular, with ethylene vinyl alcohol copolymers, molding of the mold itself is facilitated and a mold of stable dimensions can be obtained and the lens is endowed with stable water wetting properties. The ethylene vinyl alcohol copolymerization resins that can be used are marketed as "Soalite," which is manufactured Nihon Gosei Kagaku Industrial Company (Ltd.) or "Ebal," which is manufactured the Kuraray Company (Ltd.). An ethylene copolymerization ratio of various grades of approximately 25 to approximately 50 mol% can be used in this invention.

[0038] The method of polymerization should be a method in which polymerization is effected by irradiation of ultraviolet rays with a photopolymerization initiator present in the monomer mixture or a method in which polymerization is effected using azo compounds and organic peroxides. To cite examples of the photopolymerization initiators that are used, the use of benzoin ethyl ether, benzyl dimethyl ketal,  $\alpha$ ,  $\alpha'$ -diethoxyacetophenone, organic peroxides such as benzoyl peroxide and t-butyl peroxide and azo compounds such as azobisisobutyronitrile and azobisdimethyl valeronitrile may be employed.

[0039]

[Embodiments of the invention] We shall now describe this invention on the basis of working examples. This invention is not limited in any way by these examples of synthesis and working examples.

[Example of synthesis 1] 1.8 mmol of silicone manufactured by Shin-Etsu Chemical Industries (Ltd.) both terminals of which were modified by carbinol (KF6003), 36 mmol of hexamethylene diisocyanate (HMDI) modified polyethylene glycol 600 (DPEG600), and, as a catalyst, 10 mg of dibutyltin dilaurate, were dissolved in 200 g of acetone. Reflux was performed for 2 hours in a nitrogen gas flow. After cooling, 80 mmol of glycerol dimethacrylate (G-101P) manufactured by the Kyoie Chemical Company (Ltd.) was added to the reaction solution and the mixture was heated overnight at  $40^\circ\text{C}$ . 150 g





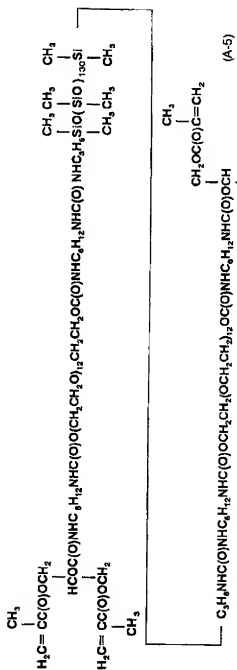




[0044]

[Example of synthesis 5] 1.8 mmol silicone manufactured by the Chisso Company (Ltd.) both terminals of which were modified with amine (FM3325), 36 mmol of DPEG600, and 10 mg of dibutyltin dilaurate were dissolved in 200 g of methyl ethyl ketone and reflux was performed for 2 hours in a nitrogen gas flow. After cooling, 80 mmol of G-101P was added to the reaction solution and the mixture was heated overnight at 40°C. It was purified by the same method as in Example of Synthesis 1 and the target compound (A-6) was obtained. The yield was 80%.

[Chemical Formula 61]

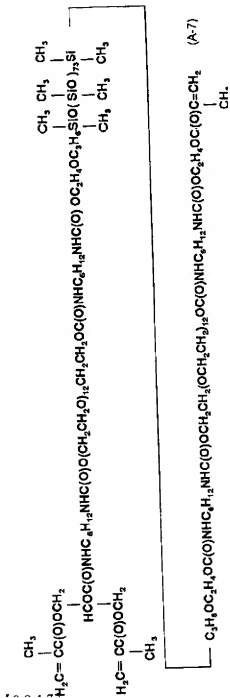




[0046]

Example of synthesis 7] 1.8 mmol of KF6003 and 36 mmol of DPEG600 were reacted by the same method as in Example of Synthesis 1, after which 40 mmol of G101P and 40 mmol of 2-hydroxyethyl methacrylate (HEMA) were reacted and the target compound (A-7) was obtained. The yield was 85%.

[Chemical Formula 63]

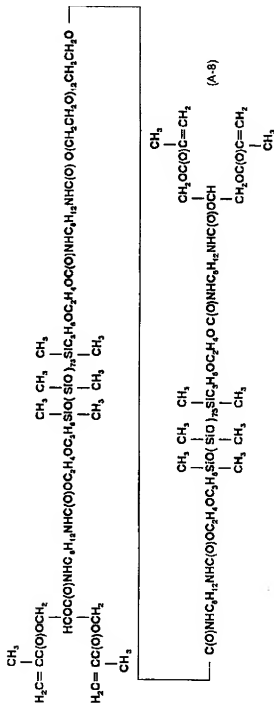




[0047]

[Example of synthesis 8] 20 mmol of KF6003, 1 mmol of DPEG600 and 20 mg of dibutyltin dilaurate were dissolved in 500 g of acetone. Reflux was performed for 2 hours in a nitrogen gas flow, after which 40 mmol of hexamethylene diisocyanate was added and the mixture was heated overnight at 40°C. It was purified by the same method as in Method of synthesis 1 and the target compound (A-8) was obtained. The yield was 62%.

[Chemical Formula 64]





[0049]

[Working Example 1] 80 parts by weight of synthesized hydrophilic polysiloxane monomer (A-1), 20 parts by weight of N,N-dimethyl acrylate and 0.5 parts by weight of 2,4,6-trimethyl benzoyl phenyl phosphine oxide were dissolved in 80 parts by weight of 2-butanol and were mixed by stirring, after which the mixed monomer solution was poured into a mold for contact lens molding made of ethylene vinyl alcohol resin (Soalite S). The solution was irradiated with ultraviolet rays for 1 hour in a photo-irradiation device and a lens-shaped polymer was obtained. The lens was immersed overnight in ethanol, after which it was immersed for 3 hours in water at 90°C, with a soft, transparent lens being obtained.

[0050] Evaluations of the physical properties of the lens that was obtained were performed by the following methods.

(1) Optical transparency

By visual observation. Cases in which there was no cloudiness and in which there was good transparency were scored O, cases in which there was cloudiness and the lens was semitransparent were scored Δ, and cases in which the lens was not transparent were scored ×.

(2) Water wetting properties

Evaluations of wetting properties were made by visual observation relative to pure water. The lens was immersed in purified water for 24 hours, after which it was withdrawn perpendicularly. When the water film was maintained for 5 seconds or longer, water wetting capacity was scored O, when the film was maintained for 1 to 5 seconds, it was scored Δ, and when it was maintained for less than 1 second, it was scored ×.

[0051] (3) Contact angle

The contact angle between the surface of the material and water drops was measured at 25°C using a contact angle measurement device (Model CA-DT manufactured by Kyowa Kaimen Kagaku (Ltd.).

(4) Water content ratio

The lens was allowed to stand for 72 hours at 37°C in physiological saline solution, after which the lens was withdrawn, the water attached to the surface was wiped off and it was weighed. Next, the lens was dried in a vacuum at 80°C until a constant weight was attained. The water content ratio was found from the change in weight by the following formula.

$$\text{Water content ratio (\%)} = (\text{weight change/weight before drying}) \times 100$$

[0052] (5) Oxygen permeation coefficient

Determinations were made by the electrode method using a Model K-316-IPI film oxygen permeation measurement device manufactured by Rika Seiki Kogyo (Ltd.) on the basis of the contact lens Koki Standard Dk Value Measurement Method. The test material strip was made with a mold into a lens of a diameter of approximately 14 mm and a thickness of approximately 0.1 to 0.5 mm and was supplied for measurement. Measurements were made in physiological saline solution at 35°C. The oxygen permeation coefficient was found from the slope of the quantity of oxygen permeation relative to test material thickness. The unit was expressed as  $(\text{ml} \cdot \text{cm}/\text{cm}^2 \cdot \text{sec} \cdot \text{mmHg}) \times 10^{-11}$ .

(6) Tensile strength

Determinations were made in physiological saline solution at 25°C using an AGS-50B universal testing machine manufactured by Shimadzu (Ltd.). The lens was cut out to a width of 3 mm at the center and its strength at the time of breaking was found. The unit was (MPa).

[0053] (7) Lipid attachment

One lens was immersed in 10 ml of 0.1% triolefin (phosphoric acid buffer solution) suspension and the solution was stirred for 2 hours at 40°C. Washing was performed in 5 ml of purified water, with shaking and washing for 30 seconds being repeated 5 times. The lens was dried in a vacuum, extraction was performed with acetone, coloration was effected with the triglyceride test reagent Triglyceride G-Test Wako manufactured by Wako Junyaku Kogyo (Ltd.) and absorbance at 505 nm was determined with an absorption spectrophotometer (Model V-550 manufactured by Nihon Bunko (Ltd.)). The quantity of attached lipid per 1 lens was found from a calibration curve that had been found separately. The results of the evaluations are shown in Table 1.

[0054]

[Working Examples 2 to 8] Contact lenses were made with the same compositions as in Working Example 1 using the hydrophilic polysiloxane monomers (A-2 ~ A-8) that were synthesized and their physical properties were evaluated. The results are shown in Table 1.

[Working Example 9] 60 parts by weight of hydrophilic polysiloxane monomer (A-1) that was synthesized, 30 parts by weight of N-vinyl pyrrolidone, 10 parts by weight of 3-tris (trimethylsiloxy) silyl propyl methacrylate and 0.5 parts by weight of 2,4,6-trimethyl benzoyl diphenyl phosphine oxide were dissolved in 60 parts by weight of tetrahydrofuran and were mixed by stirring, after which a contact lens was made by the same method as in Working Example 1 and its physical properties were evaluated. The results are shown in Table 1.

[0055]

[Working Example 10] 50 parts by weight of hydrophilic polysiloxane monomer (A-1) that was synthesized, 15 parts by weight of N-vinyl-N-acetamide, 20 parts by weight of 3-tris (trimethylsiloxy) silyl propyl methacrylate, 1 part by weight of ethylene glycol dimethacrylate and 0.5 parts by weight of 2,4,6-trimethyl benzoyl diphenyl phosphine oxide were dissolved in 50 parts by weight of tetrahydrofuran and were mixed by stirring, after which a contact lens was made by the same method as in Working Example 1 and its physical properties were evaluated. The results are shown in Table 1.

[0056]

[Comparative Example 1] A contact lens was made in the same way as in Working Example 1 using silicone (FM7721) manufactured by the Chisso (Ltd.) Company of which both terminals were methacryl modified and its physical properties were evaluated. The results are shown in Table 1.

[Comparative Example 2] A contact lens was made with the same composition as in Working Example 1 using the hydrophilic polysiloxane monomer (B-1) that was synthesized and its physical properties were evaluated. The results are shown in Table 1.

[0051]

[Table 1]

Table 1

	Hydrophilic siloxane monomer	Transparency	Water wetting property	Contact angle (°)	Water content ratio (%)	Oxygen permeability coefficient (ml · cm/cm <sup>2</sup> · sec · mmHg)	Tensile strength (MPa)	Amount of lipid attachment (μg/lens)
Working Example 1	A-1	O	O	69	34	78	3.8	0.1
Working Example 2	A-2	O	O	75	30	80	4.3	0.2
Working Example 3	A-3	O	Δ	89	27	75	3.0	0.5
Working Example 4	A-4	O	O	70	30	66	5.1	0.1
Working Example 5	A-5	O	O	65	32	79	3.8	0.3
Working Example 6	A-6	O	O	65	40	42	2.2	0.1
Working Example 7	A-7	O	O	60	37	243	3.0	0.4
Working Example 8	A-8	O	Δ	92	18	281	2.0	1.1
Working Example 9	A-1	O	O	58	42	92	3.0	1.6
Working Example 10	A-1	O	O	58	38	120	3.9	2.0
Comparative Example 1	FM7721	x	x	110	9	320	1.0	10.8
Comparative Example 2	B-1	O	O	58	35	310	0.7	5.6

[0058]

[Effect of the invention] The copolymers of which the hydrophilic polysiloxane monomers of this invention are components are substances of superior strength, surface hydrophilicity, high oxygen permeability, contamination resistance, softness, optical transparency and strength and are useful as lens material for ophthalmologic use such as contact lenses.

[Brief Explanation of the Figures]

[Figure 1] This is the NMR spectrum of Example of Synthesis (A-1).

[Figure 2] This is the IR spectrum of Example of Synthesis (A-1).

[Figure 2]

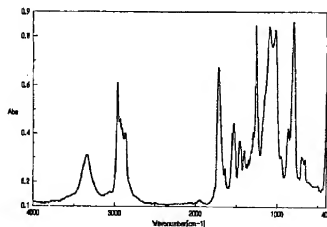


Figure 2. IR spectrum of Example of Synthesis (A-1)

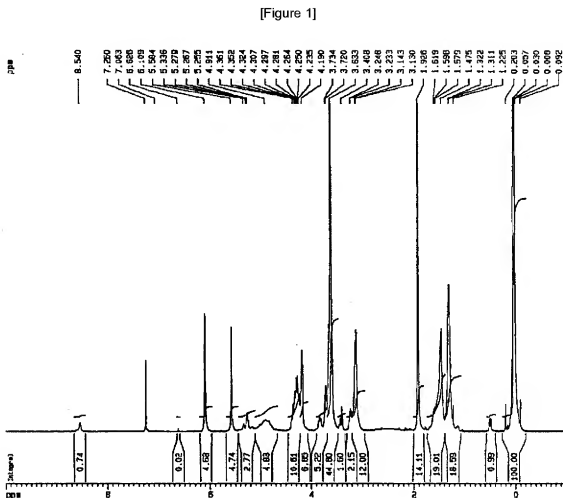


Figure 1. NMR spectrum of Example of Synthesis (A-1)

Continued from front page

(51)	Int.Cl. <sup>7</sup>	Ident. Symbols FI	Topic Code (Reference)
G02C	7/04	G02C	7/04
// B29K	83:00	B29K	83:00
B29L	11:00	B29L	11:00
C08L	83:12	C08L	83:12

F Terms (Reference)	2H006	BB01	BB05	BB07		
	4F071	AA51X	AA53X	AA67X	AA75X	
		AF04	AF08	AF30	AH19	BA02
		BB01	BC01	BC03		
	4F204	AA21E	AA33	AA33E	AA33L	
		AB04	AH74	EA03	EA04	EB01
		EE02	EF01	EF27	EK18	
	4J027	AC03	AC08	AC09	AF01	AF03
		AF04	AF05	AF06	BA14	BA18
		BA19	BA20	BA23	BA24	BA26
		CB03	CB04	CC05	CD04	
	4J035	BA02	CA071	CA101	CA131	
		GA08	GB05	GB09	LA03	LB20